Domain formation in lead titanate ferroelectric thin films

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Domain formation in lead titanate ferroelectric thin films

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Abstract — Epitaxial lead titanate ferroelectric thin films were grown on strontium titanate(001) and dysprosium scandate(110) substrates by RHEED controlled pulsed laser deposition. We used high resolution transmission electron microscope to investigate the structure of the films. The clear difference in the shape of the a-domains were observed in films on the two different substrates. Films on strontium titanate substrates were found to have wedge shaped *a*-domains whereas, *a*-domains in the films on the dysprosium scandate substrates were found to have nearly uniform width. The difference in the shape of *a*-domains is attributed to the difference in stiffness of the two substrates. Nanoindentations on the substrates were performed to quantify their the stiffness. In another set of experiment we have successfully grown completely c-oriented lead titanate thin films with various thicknesses ranging from 22-340 nm on strontium titanate substrates. Laser pulse frequency (growth rate) is the crtical parameter for the formation of *a*-domain free lead titanate films. The strontium titanate substrate surface termination is also important at higher growth rates.

INTRODUCTION

Ferroelectrics have been widely studied, because of their potential application in various memory devices, sensors and actuators, MEMS etc.. The last few decades research has focussed mainly on $PbTiO_3$, $BaTiO_3$, $Pb(Zr_{1-x}Ti_x)O_3$, $BaSr_{1-x}Ti_xO_3$. Particularly thin films of $PbTiO_3$ have been studied after growing them on different substrates like MgO, $SrTiO_3$, $KaTaO_3$, $LaAlO_3$. Although a lot of progress has been made, 90° domain formation is still a persistent problem at least for thicker films due to the difference in film-substrate lattice mismatch, and also cubic paraelectric to tetragonal ferroelectric phase transistion [1-3]. In this work we have focussed our attention mainly on the shape of the *a*-domains in the $PbTiO_3$ thin films grown on two different substrates namely $SrTiO_3$ and $DyScO_3$. There is no previous literature available on this topic. From an application point of view it is generally desired to have films with their *c*-axis oriented normal to the substrate surface, so that the spontaneous polarization is normal to the surface. Completely c-oriented single crystal $PbTiO_3$ thin films on $SrTiO_3$ grown by the PLD have not been reported yet, at least not for thicker films of a few hundred nanometers. By sputtering [4] and CVD [5] completely c-oriented films could be grown, but in the former case only for (0.9° - 1.7°) miscut substrates and in the latter case only below 150 nm thickness. Here, we show that we can grown 340 nm thick completely c-oriented films on 0.2° miscut substrates. We have employed AFM, XRD and TEM for investigating the shape of *a*-domains and also to analyse completely c-oriented films.

EXPERIMENTAL

Pulsed-Laser Deposition was used to grow $PbTiO_3$ films (with various tickness') on (001)$SrTiO_3$ and two 30 nm films on (110)$DyScO_3$ with 5 nm and 30 nm $SrRuO_3$ conductive perovskite as intermediate layer. The $SrTiO_3$ substrates were treated chemically in order to induce a TiO_2 termination. AFM measurements were performed to determine mixed or single SrO/TiO_2 termination occurred. $DyScO_3$ substrates were only treated thermally before deposition. $PbTiO_3$ films were deposited on $SrTiO_3$ at a temperature of 570 °C using a pulsed KrF excimer laser at a wavelength of 248 nm (Lambda physik COMPex pro 205) in a default ambient oxygen pressure of 0.13 mbar with a repetition rate between 0.5 and 15 Hz. The substrates were kept at a distance of 51 mm from the target. An energy density of 2.5 J/cm^2 with a laser spot of ~3 mm^2 was used. After deposition the films were annealed within oxygen of 0.5 bar and cooled generally at a rate of 5 °C/min. The films on $DyScO_3$ were deposited with a slightly less energy density of 2 J/cm^2 and a substrate target distance of 45 mm with a repetition rate of 1 Hz; the other parameters were identical as for $PbTiO_3$ growth on $SrTiO_3$. The intermediate $SrRuO_3$ layer was grown at a temperature of 600° C with 2 Hz repetition rate.

XRD measurements (X'Pert Panalytical, Cu anode λ=1.540598Å) were used to study the phase, presence, amount and tilting of *a*-domains. By performing measurements on both the θ-2θ ($K_{//}$) and ω ($K_{\perp}$) axes, reciprocal space maps were obtained.

TEM samples were prepared by the conventional method involving cutting, grinding, polishing, dimpling and ion milling. A precision ion polishing system (Gatan model 691) with 4kV Ar+ beams having incident angle of 8° on both sides was used. The observations were performed with a JEOL 2010F electron microscope operating at an accelerating voltage of 200 kV. Nanoindentations experiments were performed with a calibrated MTS Nano Indenter® XP with a Continuous Stiffness Module (CSM).

At room temperature the following lattice parameters hold. The bulk lattice parameters of $PbTiO_3$ are $a = b =$ 3.894 Å, c = 4.140 Å [6], i.e. with a tetragonal structure. $SrTiO_3$ has a cubic structure and its lattice constant is a = 3.905 Å. The $DyScO_3$ has an orthorhombic structure with the following lattice constants: a = 5.440 Å, b = 5.713 Å,

c = 7.887 Å [7]. (110)-oriented $DyScO_3$ has nearly a square in-plane lattice with $a_{//}$ = 3.944 Å.

RESULTS AND DISCUSSION

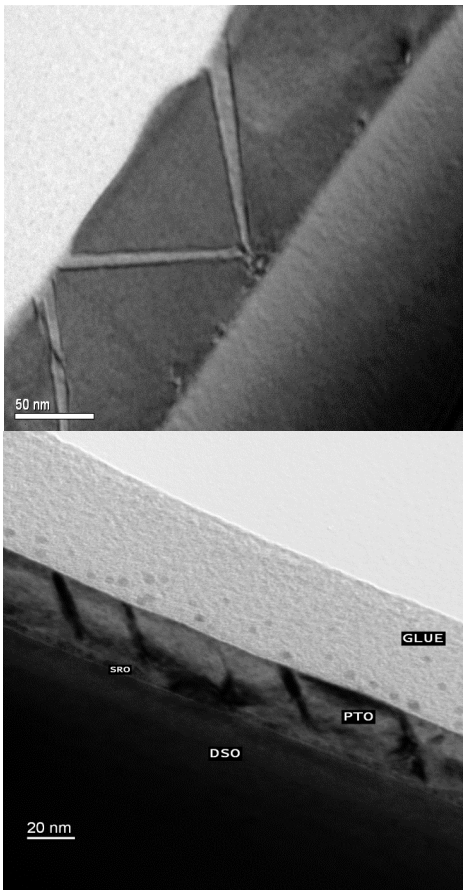
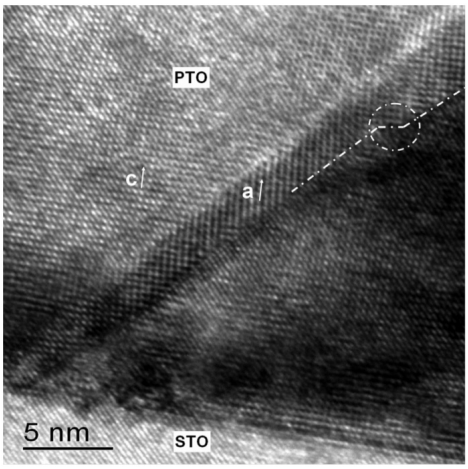


Fig.1. Bright-field TEM images of $PbTiO_3$ films (top) 110 nm film on $SrTiO_3$ showing the presence of wedge-shaped *a*-domains (bottom) 30 nm $PbTiO_3$ film on $DyScO_3$ (with 5 nm intermediate $SrRuO_3$ layer) showing the presence of a nearly regularly spaced array of *a*-domains within the $PbTiO_3$ film.

A cross-sectional bright field TEM image of a 110 nm $PbTiO_3$ film on $SrTiO_3$ is shown in Fig.1a. The presence of wedge shaped *a*-domains, with decreasing widths when approaching the substrate, can be observed clearly in the image. A bright-field TEM image of the sample with the 30 nm $PbTiO_3$ and 5 nm intermediate $SrRuO_3$ layer is shown in Fig1b. High resolution TEM images of the films on both substrates also indicate differences; see Fig 2. In general, the domain walls of the *a*-domain tend to be quite parallel for $PbTiO_3$ on $DyScO_3$. The domains have clearly less wedge shape than in case of the $SrTiO_3$ substrate. We observed that, in case of only 5 nm intermediate $SrRuO_3$ layer, steps in the domain wall are present, whereas such steps were not detected in case of the 30 nm $SrRuO_3$ layer (Fig.2b). The c/a ratio within the $PbTiO_3$ derived from HRTEM images of *c*-domains is 1.07 (±0.01) which is in agreement with the theoretical value of 1.063. We obtained 3.8° for the tilt between the unit cells in the *a*- and *c*-domains which is also close to the theoretical value of 3.5°. For the *c*-domains the (001) plane is parallel to the interface, but for the *a*-domains in principle the tilt of 3.5° holds between the substrate surface and the (100) (or (010)) plane. The 'defect' accounting for this local misorientation can in analogy be called a misfit disclination [8-10].

The strains associated with this disclination create the tendency to minimize the width of the *a*-domains. However, for strain accommodation within the film *a*-domains are required. Overall, a strain-energy balance will hold. In fact, this balance will prevent the formation of *a*-domains below a critical thickness in accordance with theory [11] and experiments [12]. Above the critical thickness these domains can develop, but nevertheless the interface strains will tend to keep the domains in most cases thinner near the interface than in the bulk. To minimize domain-wall energy in principle thick *a*-domains would be expected, but these are not found due to the interfacial clamping strain. Clearly away from the interface the *a*-domains have the tendency to have a width corresponding to $c/\sin\alpha$ where α is the tilt mentioned above (which is $90° - 2\tan^{-1}(c/a)$). In this way the planes parallel to the interface in the *c*-domains on both sides of the *a*-domain match coherently with the slightly tilted plane in the *a*-domain [12]. If the clamping strain energy at the interface of an *a*-domain is higher than the strain energy associated with steps in the domain wall, then a wedge-shaped *a*-domain with smaller width near the interface will result. Apparently this situation holds in case of the $SrTiO_3$ substrate. In case of $DyScO_3$ with $SrRuO_3$ as intermediate layer the interface clamping strain energy is apparently less and the steps in the domain wall tend to run all the way to the interface and form domains with nearly uniform width. This difference in clamping strain energy is due to a difference in stiffness of the substrate, where a higher stiffness causes more strain energy.

Indeed, this analysis appears consistent, because with nanoindentation measurements we found the following values for the Young's modulus: $SrTiO_3$ 279±2 GPa, $DyScO_3$ 250±3 GPa and $SrRuO_3$ 161 GPa [13].



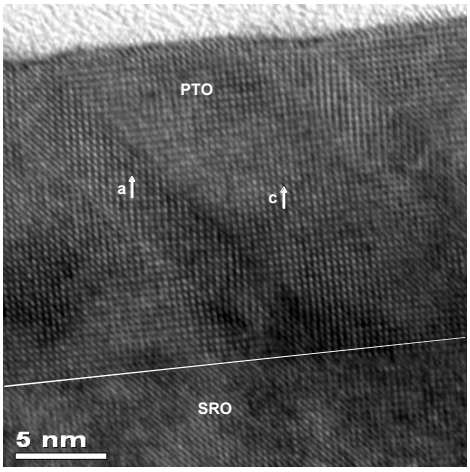


Fig.2. High-Resolution TEM images of $PbTiO_3$ films. (top) 110 nm film on $SrTiO_3$ shows steps within the domain wall (bottom) Two closely spaced *a*-domains with uniform width of about 5 nm in the $PbTiO_3$ film on $DyScO_3$ with 30 nm intermediate $SrRuO_3$ layer.

Based on these considerations it can now be understood that the *a*-domains in the $PbTiO_3$ on the 30 nm $SrRuO_3$ showed most uniform width, because they make use of the most compliant $SrRuO_3$ in reducing the stress fields in $PbTiO_3$ and that in case of the 5 nm $SrRuO_3$ film a higher step density in the domain walls is found (because the *a*-domains also experiences the stiffer $DyScO_3$), but the domains are most clearly wedge-shaped in case of $SrTiO_3$ being the stiffest material of the three.

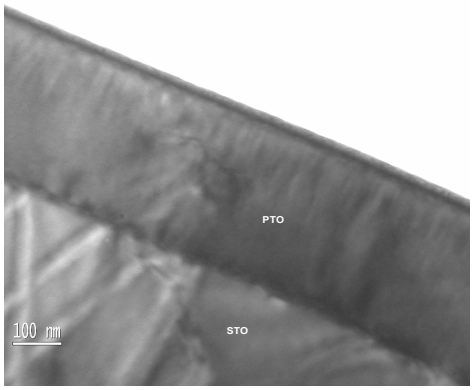


Fig3. Bright field TEM image of completely c–axis oriented $PbTiO_3$ film of ~340nm on $SrTiO_3$.

We have sucessfully grown completely c-axis oriented thick $PbTiO_3$ on $SrTiO_3$. These $PbTiO_3$ films ranged in thickness from 22-340 nm. The $PbTiO_3$ films were grown with changing parameters like laser pulse frequency (growth rate), cooling rate, oxygen-partial pressure and substrate (termination) treatment. At low laser pulse frequencies (≤ 5 Hz) *a*-domains did not develop up to large thickness (larger than 250-340 nm) independent of the quality of the substrate treament (i.e. fraction of TiO_2 termination), oxygen partial pressure and cooling rate. At high laser pulse frequencies (≥8 Hz) a-domains develop above critical thickness (typically between 20-100 nm) even for perfect 100% TiO_2 terminated substrates. In these cases secondary phase were generally detected (XRD/TEM) which are excpected to act as nucleation sites for *a*-domain formation. At intermediate laser pulse frequencies (in between 5 and 8 Hz) *a*-domain formation can be avoided up to larger thicknesses (>250 nm) when the substrate has perfect TiO_2 termination; with poorly treated substrates (mixed termination) *a*-domains did occur.

According to K.Wasa et al. [4] a step flow growth mode helps to grow completely c-axis oriented $PbTiO_3$ films of 260 nm on $SrTiO_3$ substrates. Indeed this step flow growth mode was induced by a critical miscut of the $SrTiO_3$ substrate ranging from 0.9° - 1.7°. However, in our case all the films were grown on 0.2° miscut substrates and we obtain 340 nm thick $PbTiO_3$ film without formation of any *a*-domain. The reciprocal space maps from the X-ray diffraction data (not shown) and TEM (cf. Fig. 3) confirm the absence of *a*-domains. Although our deposition temperature is above the Curie temperature of bulk $PbTiO_3$ (i.e. the cubic paraelectric phase should grow), the absence of *a*-domains indicate that our films were directly grown in the tetragonal (ferroelectric) phase, which is in good agreement with the recent work reported by Janolin et al. [14].

CONCLUSIONS

Domain structures of c/a/c type in $PbTiO_3$ thin films have been investigated with the help of HRTEM. The *a*-domains in the films on the $SrTiO_3$ substrate have a clear wedge shape. The *a*-domains on the $DyScO_3$ substrates have uniform width. The difference in the shape of *a*-domains in the films was attributed to the difference in stiffness between $SrTiO_3$ and $DyScO_3$ substrates, which is in agreement with our nanoindentation measurement on these substrates.

Completely c-axis oriented $PbTiO_3$ films of thickness up to 340 nm were grown on $SrTiO_3$ substrates by pulsed laser deposition under different growth conditions. Predominantly the laser pulse frequency (growth rate) but also the substrate termination clearly influence the growth of single crystalline single domain $PbTiO_3$ thin films on $SrTiO_3$ substrates. Piezo-response Force Miscroscopy investigations of the functional properties ofthese systems are in progress.

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